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National Inventory of Sources and Emissions of Manganese (1972)

Internal
Report APCD 75-6

Air Pollution
Control Directorate
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NATIONAL INVENTORY OF SOURCES AND EMISSIONS OF MANGANESE (1972)*

Pollution Data Analysis Division
Air Pollution Programs Branch
Air Pollution Control Directorate

Report APCD 75-6

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*This report is based on a study undertaken for the Department of the Environment by Surveyer, Nenniger and Chênevert Incorporated, Montreal, Quebec, under Contract No. OSR3-0526.

ABSTRACT

Atmospheric emissions of manganese from various Canadian sources have been estimated for the year 1972. The data presented in this report are summarized in Table 1 and Figures 1 and 2. Total emissions of manganese to the atmosphere in 1972 are estimated at 6625 tons. The largest contributor is the ferroalloy industry which accounts for 62% of the total. Emissions from the primary iron and steel industry account for a further 37%. On a geographic basis Ontario accounts for 65% of total Canadian manganese emissions followed by Quebec with 23%.

Results are first approximations due to paucity of data. The inventory serves to place the various emission sources in perspective and the reader is cautioned not to use emission estimates out of context of this inventory.

RÉSUMÉ

On a fait l'estimation des émissions de manganèse dans l'atmosphère en 1972 par les différentes sources canadiennes. Le tableau 1 et les figures 1 et 2 résument les données contenues dans le présent rapport. Les émissions ont été estimées à 6625 tonnes, dont 62% sont attribuables à l'industrie des ferro alliages tandis que 37% proviennent de l'industrie du fer et de l'acier de première fusion. L'Ontario contribue à 65% des émissions et se classe au premier rang, suivie du Québec avec 23%.

Étant donné le peu de données disponibles ces chiffres constituent une première approximation. L'inventaire de ces émissions a pour but de déterminer l'importance relative des diverses sources d'émissions; on invite donc le lecteur à ne pas utiliser ces valeurs estimatives hors contexte.

TABLE 1 MANGANESE EMISSIONS BY PROVINCE AND SECTOR, 1972 (tons)

Sector	Province										
	B.C.	Alta.	Sask.	Man.	Ont.	Que.	Nfld.	Maritimes	N.W.T. Yukon	**Total Canada**	% Total
INDUSTRY											
Ferroalloy and manganese alloy plants	-	-	-	-	2839	1234	-	-	-	**4073**	61.5
Primary copper and nickel production	-	<1	-	4	12	6	-	-	-	**22**	0.3
Primary zinc production	4	-	-	3	2	3	-	-	-	**12**	0.2
Primary iron and steel production	13	69	378	96	1391	245	-	232	-	**2424**	36.6
Iron and steel foundries	2	<1	<1	1	23	9	<1	1	-	**36**	0.6
Miscellaneous sources	<1	<1	<1	<1	8	6	<1	<1	<1	**16**	0.2
FUEL COMBUSTION/ STATIONARY SOURCES											
Power generation	<1	2	3	1	<1	<1	<1	2	<1	**8**	0.1
Industrial and commercial	<1	1	<1	1	4	2	<1	1	<1	**11**	0.2
Domestic	← N* →				<1	<1	← N →			<1	<0.1
TRANSPORTATION	← N →									**N**	**N**
SOLID WASTE INCINERATION	-	-	<1	1	4	2	-	1	-	**8**	0.1
PESTICIDE APPLICATION	2	2	2	2	2	2	1	2	-	**15**	0.2
TOTAL	**22**	**74**	**384**	**109**	**4285**	**1509**	**2**	**239**	**1**	**6625**	
% TOTAL	0.3	1.1	5.8	1.7	64.7	22.8	<0.1	3.6	<0.1		100.0

*N-negligible

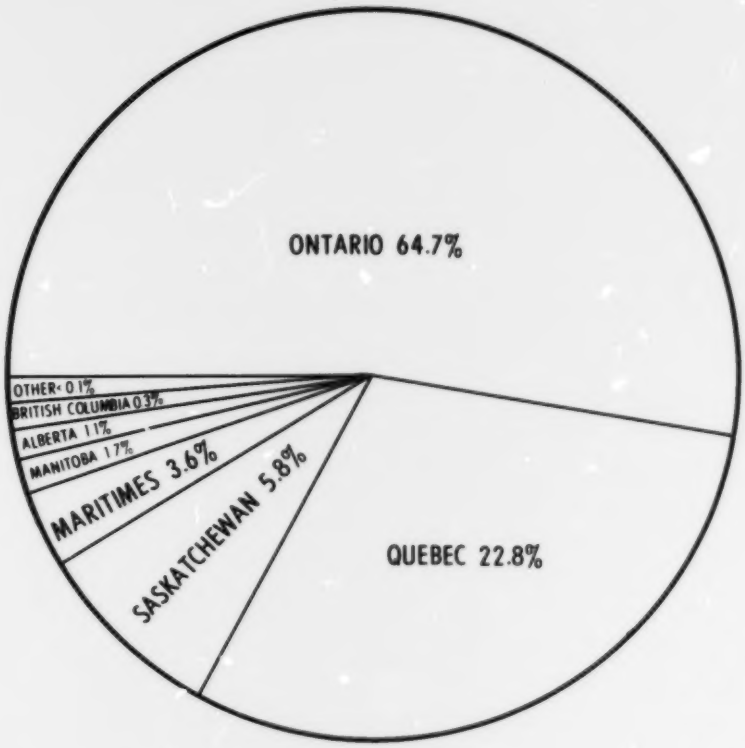

FIGURE 1 PERCENT MANGANESE EMITTED BY PROVINCE, 1972

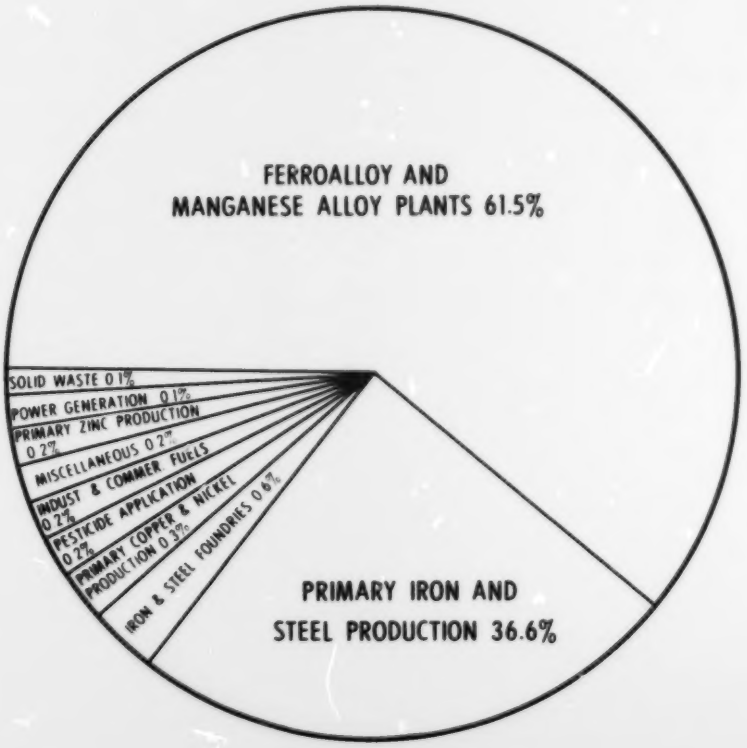

FIGURE 2 PERCENT MANGANESE EMITTED BY SOURCE, 1972

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1 INTRODUCTION

1.1 Scope

The purpose of this report is to identify and quantify sources of atmospheric emissions of manganese in Canada for the year 1972. Information contained in this report was obtained from a literature survey, a computer search conducted at the National Science Library, and from previous inventory studies. Information was also gathered from a specifically designed questionnaire which was sent to approximately 1050 plants and received a response of 51%. Details on response rate and quality of returns are given in the Appendix. As far as possible emission estimates were based on source testing data applicable to Canadian conditions.

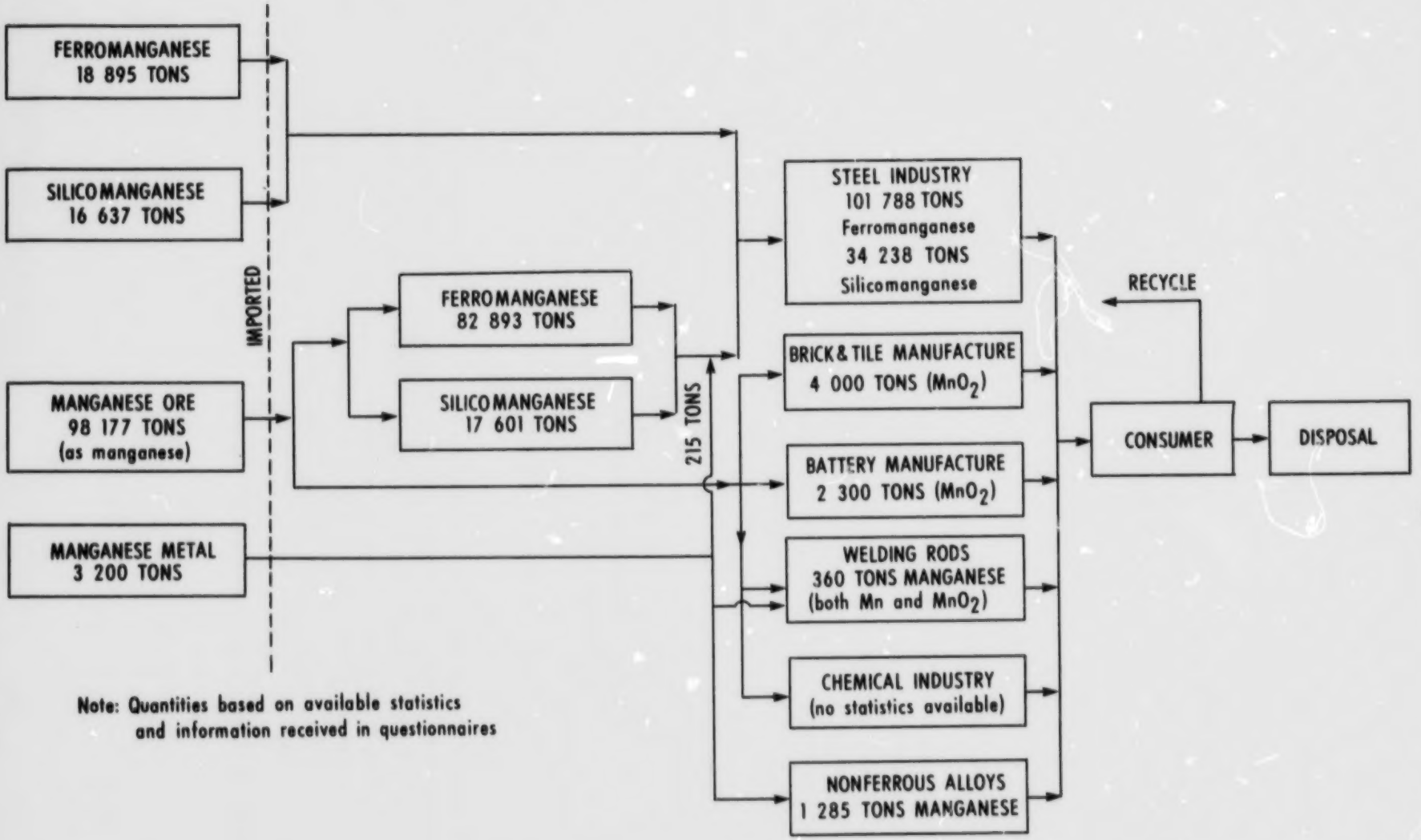
1.2 Sources and Uses of Manganese

Manganese occurs in many minerals that are widely distributed in the earth's crust but few are of economic importance. The most common sources are the minerals pyrolusite and psilomelane. Canada does not produce manganese ore, because known deposits contain insufficient tonnages of adequate quality; however, in 1972 Canada imported 98 177 short tons of manganese (as elemental manganese) in ores and concentrates, 18 895 tons of ferromanganese and 16 637 tons of silicomanganese. Ferromanganese and silicomanganese are used principally in iron and steel production.

Most manganese ores imported into Canada are of the metallurgical grade and are processed into manganese ferroalloys for use in the iron and steel industry. Ores having a manganese to iron ratio of 7:1 or more are preferred for making ferromanganese because they enable a high productive capacity to be maintained in a ferroalloy plant. Manganese is required in steelmaking chiefly to counteract the effects of sulphur; however, it also has some deoxidizing power and when added in certain proportions, can act to harden and reduce the plasticity of steel (1). Manganese ore is also used in battery production. Ores for this purpose are subject to chemical and physical specifications, the principal requirement being a high manganese dioxide content.

The quantity of manganese chemicals manufactured in Canada in 1972 is assumed to be small (2, 3). Manufacturers of manganese chemicals use manganese ores of various grades including high-grade ores and concentrates also suitable for metallurgical use. These are used to make manganese chemicals such as potassium permanganate, sulphates, and chlorides for use in the welding rod, glass, dye, paint and varnish, fertilizer, pharmaceutical and photographic industries (1). Manganese ore is also used as an oxidizing agent in the manufacture of hydroquinone (4), and ores of various grades are used in the manufacture of electrolytic manganese metal.

Figure 3 identifies the uses and sources of manganese.



Note: Quantities based on available statistics and information received in questionnaires

FIGURE 3 SOURCES AND USES OF MANGANESE, 1972

2 INDUSTRIAL EMISSIONS

2.1 Ferroalloy and Manganese Alloy Plants

Two companies produced ferromanganese and silicomanganese in Canada during 1972, consuming a major portion of the manganese ore used in Canada.

2.1.1 ***Process Description.*** Ferromanganese and silicomanganese may be produced by smelting in either a blast furnace or an electric furnace. The furnaces used in Canada are open-top electric furnaces but one company reported converting to sealed furnaces. These sealed furnaces began operation in October 1973.

The majority of ferroalloy furnaces are termed submerged arc, although the mode of energy release in many cases is resistive heating. Raw ore, coke, limestone or dolomite, and sometimes fluorspar, mixed in proper proportions constitute the charge for the electric-arc furnace process. The furnace is lined with carbon and has intense heat zones (2200°C-2760°C) near the arc to effectively complete oxide reduction. A large supply of electric power is necessary for economical operation. Operating considerations include power and electrode requirements, size and type of furnace, amount and size of coke, and the nature of slag losses.

Submerged-arc furnaces generally operate continuously except for periods of power interruption or mechanical breakdown. Operating time averages 90 % - 98 %. The electrodes operate 3 ft-6 ft above the hearth, and are submerged 3 ft-5 ft below the mix level so that some heat exchange and mass transfer can occur between the reaction gas and the mix. The products of these furnaces, such as ferromanganese, silicomanganese and slag, are intermittently tapped into a settler (5).

2.1.2 ***Emissions.*** The electric smelting furnace is a major source of air pollution. The conventional submerged-arc furnace uses carbon reduction of metallic oxides and continuously produces large quantities of carbon monoxide. Other sources of gas are moisture in the charge materials, reducing agent volatile matter, thermal decomposition products of the raw ore, and intermediate products of reaction. Carbon monoxide normally accounts for about 70% of the gas volume. Gases rising from the furnace carry fume or fume precursors and also entrain fine constituents of the mix or charge. Because submerged-arc furnaces operate in steady state, gas generation is continuous.

In open furnaces, all the carbon monoxide burns with induced air at the top of the charge, resulting in a large volume of gas. Fume emission also occurs at furnace tap holes. Because most furnaces are tapped intermittently, tap hole fumes only occur about 10%-20% of the furnace operating time. Fume also occurs in handling the metal after the tapping step. Conveying the ladle, pouring, and casting give rise to fumes on an intermittent basis.

Because manganese ores contain a significant amount of water, as well as manganese oxides which release oxygen upon heating at temperatures below 1000°C, a manganese furnace can be subject to 'rough' operation. Sudden gas release can result in substantial mix ejection. In furnaces with self-baking electrodes, the relatively oxidizing atmosphere can result in 'fluting' of the electrodes, furnishing a direct gas passage from the high-temperature zone of the furnace, with increased fume

emission. Silicomanganese furnaces are subject to 'slag boils,' where slag rises to cover the top surface of the charge, impeding mix delivery and uniform gas ascent.

Differences in operating technique can have a significant effect on fume generation. The average rate of furnace-gas production is roughly proportional to electrical input, so that a higher load on a given furnace generally results in at least a proportional increase in fume emission. In some circumstances, fume emission increases at a rate greater than the load increase because of rougher operation and inadequate gas withdrawal capacity.

Loads on existing furnaces have been progressively increased as operating techniques improve and more knowledge of transformer capacity becomes available. This tendency has taxed the furnace gas collection systems and, in the case of open furnaces, has presented a more concentrated source of fume.

Manganese emission estimates for the ferroalloy industry are based on published emission factors (6). The uncontrolled emission factors used in this survey are 87 lb manganese/ton of ferromanganese produced and 53 lb manganese/ton of silicomanganese produced. No emission controls are used.

Total manganese emitted to the atmosphere from ferromanganese and silicomanganese production in 1972 is estimated at 4073 tons.

2.1.3 Particle Size Distribution. No data were reported in the survey on particle size; however, a survey done in the United States (4) reports particle size of fume generated from tapping to be below 2 microns.

2.2 Primary Copper and Nickel Production

There were six primary copper smelters in Canada in 1972, three of which also produced primary nickel. One other company produced the remainder of the primary nickel and also a small amount of copper sulphide as a by-product. A small amount of copper matte was also produced as a by-product of primary lead production. In 1972, 801 690 tons of recoverable copper and 258 087 tons of nickel were produced in Canada (7, 8).

2.2.1 Process Description. The type of process and process stages required depend primarily on the characteristics and chemical composition of the ores. The most common method of producing primary copper and nickel consists of the following basic process steps:

Roasting. The concentrates are roasted to drive off most of the sulphur in preparation for subsequent smelting and converting reactions.

Smelting. In this stage the charge is melted, usually in a reverberatory furnace, where it separates into a matte and a slag.

Converting. The mattes are converted through a series of chemical reactions to the crude metals.

Anode Furnace and Electrolytic Refining. The crude copper or nickel is then cast into anodes to be refined by electrolysis.

Cathode Melting. Electrolytic copper is melted under reducing atmosphere in a shaft-type furnace and cast into billets, slabs, etc. for marketing.

Figure 4 is a typical flow diagram for the pyrometallurgical process.

Another method used for the production of nickel is the hydrometallurgical process, practiced at one plant in Canada.

2.2.2 Emissions. The main atmospheric emission points from the production of primary copper and nickel are the roasters, furnaces, and converters. Emissions from operations such as ore handling and anode furnace are negligible in comparison. Manganese is emitted primarily as manganese dioxide.

Only two companies provided estimates for manganese emissions. Estimates for the other companies are based on reported particulate emissions. Emission factors for various process stages cannot be compared, because of the difference in processes from one company to the other.

A similar survey done in the United States (4) does not report manganese emissions from primary copper and nickel production.

Total emissions of manganese to the atmosphere from primary copper and nickel production for 1972 are estimated at 22 tons.

2.2.3 Particle Size Distribution. Table 2 summarizes information received on particle size distribution for particulate emissions for primary copper and nickel smelters.

2.3 Primary Zinc Production

During 1972, 555 200 tons of primary zinc and 1538 tons of cadmium were produced in Canada by four plants.

2.3.1 Process Description. All the primary zinc in Canada is produced by the electrolytic process which consists of the following stages:

Roasting. Zinc sulphide ore is roasted to zinc oxide. The roasted ore is termed calcine and contains up to 3% sulphur.

Leaching. The calcine is leached with sulphuric acid to produce a neutral solution of zinc and other metal sulphates. The insoluble portion, which contains iron, is separated from the soluble portion and contains about 20% zinc as ferrite, when using the conventional electrolytic process.* Manganese dioxide is added in the leaching process to oxidize the iron.

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* Two plants in Canada use the Jarosite Process, which gives higher zinc recovery than the conventional method. In the Jarosite Process the insoluble portion contains up to 3% zinc as ferrite.

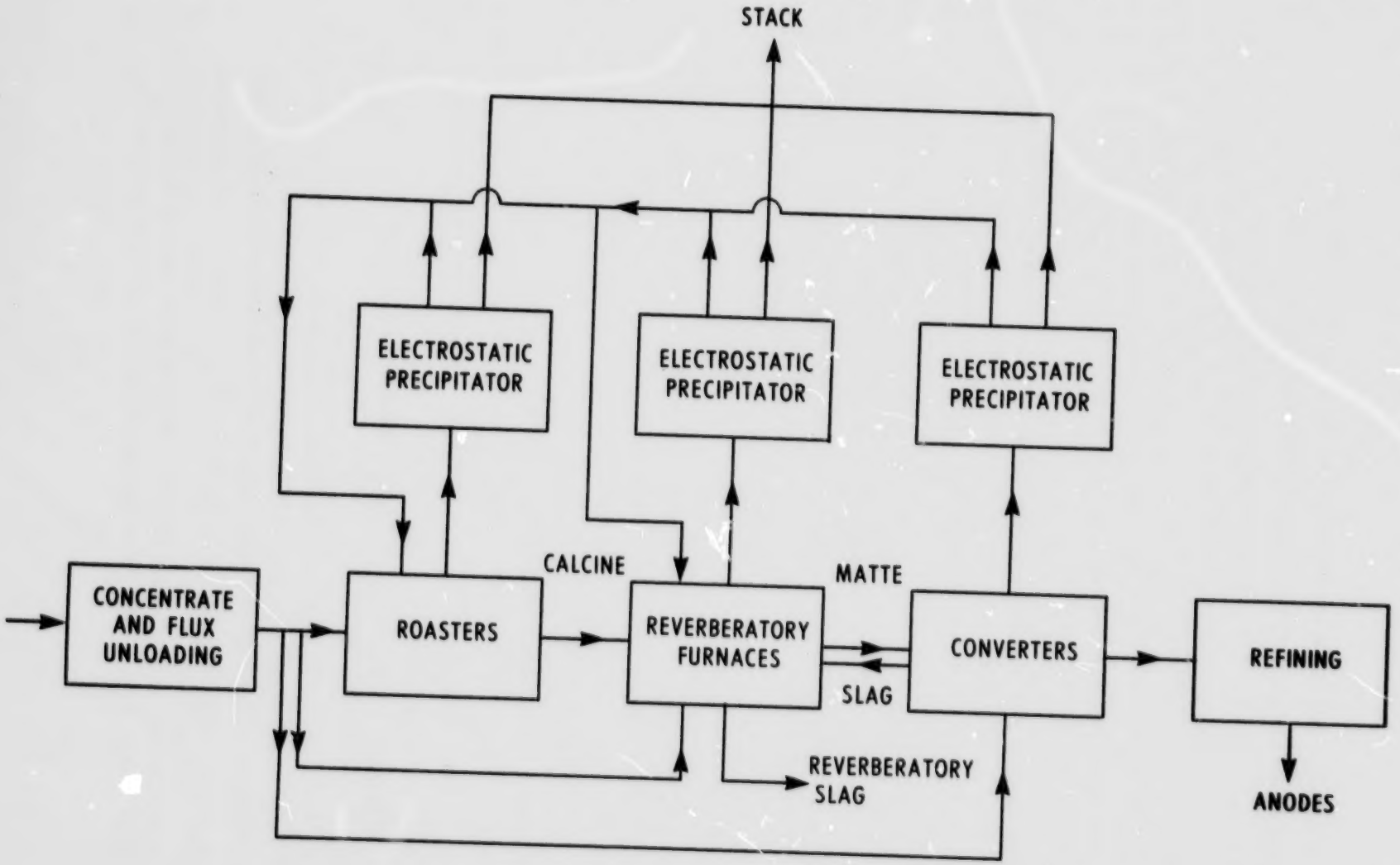

FIGURE 4 PRIMARY COPPER AND NICKEL PLANT FLOW DIAGRAM

TABLE 2 PARTICLE SIZE DISTRIBUTION FOR PARTICULATE EMISSIONS FROM PRIMARY COPPER AND NICKEL SMELTERS

Source	Particle size (microns)	Weight of particulates (%)
Sinter plant		
	> 74	10
	37 - 74	18
	0.4 - 37	38
	< 0.4	34
Smelter plant A		
	> 74	19
	37 - 74	26
	0.4 - 37	30
	< 0.4	25
Smelter plant B		
	> 45	5
	21 - 44	10
	11 - 20	20
	< 10	65
Smelter plant C		
	44 - 100	5
	10 - 44	20
	< 10	75
Smelter plant D		
	4.8 - 11.7	19
	2.1 - 4.8	27
	0.5 - 2.1	14
	< 0.5	40

Purification. Cadmium and other metals are cemented (precipitated) from the solution and the purified solution is cooled in forced draft cooling towers before going to the electrolysis plant. Arsenic trioxide and zinc dust are usually added to precipitate impurities.

Electrolysis. Zinc is plated from the solution. The temperature of the electrolyte is controlled by forced draft cooling towers.

Melting and Casting. The zinc cathodes are melted and cast into ingots.

Zinc Dust Plant. Zinc dust required for the purification step is made by melting some of the zinc followed by air atomization of the liquid metal.

Cadmium Plant. A by-product of zinc production is cadmium. It is precipitated from the solution during the purification stage and is further purified to remove copper before being melted and cast into ingots.

Figure 5 is a typical flow diagram for a zinc plant.

2.3.2 Emissions. Information from the questionnaires indicates that concentrations of manganese in the ores range from 0.10%-0.22%. All companies except one have acid plants for the production of sulphuric acid from roaster gases. Before entering the acid plant, the gases are thoroughly cleaned by cyclones, electrostatic precipitators, and in some cases acid scrubbers, to remove particulate matter. The company without an acid plant has an electrostatic precipitator to control emissions.

Manganese occurs in both the spent and neutral electrolyte solutions. Manganese is emitted to the atmosphere because of drift loss when these solutions are cooled in forced draft-type cooling towers. Solution drift is 0.003%. Small amounts of manganese were also emitted from the handling and storage of ore and manganese dioxide.

Estimates of drift loss from cooling towers is based on information from equipment suppliers. Estimates for roaster and acid plant stacks were calculated from source testing information.

A similar survey done in the United States (4) does not mention loss of manganese from primary zinc production. No other emission factors were found. The controlled emission factor calculated for this survey for a roaster without an acid plant is 0.03 lb manganese/ton zinc produced. Emissions from roasters with acid plants are negligible. The controlled emission factor for the spent and neutral electrolyte cooling towers is estimated at 0.04 lb manganese/ton of zinc produced.

Total emissions of manganese from the primary zinc industry in 1972 are estimated at 12 tons.

2.3.3 Particle Size Distribution. Information reported on particle size distribution for particulate emissions is shown in Table 3.

2.4 Primary Iron and Steel Production

There were 45 plants in Canada engaged in the production of primary iron and steel in 1972. Primary iron production capacity was about 12 million tons, and steel furnace plant capacity about 16 million tons (9).

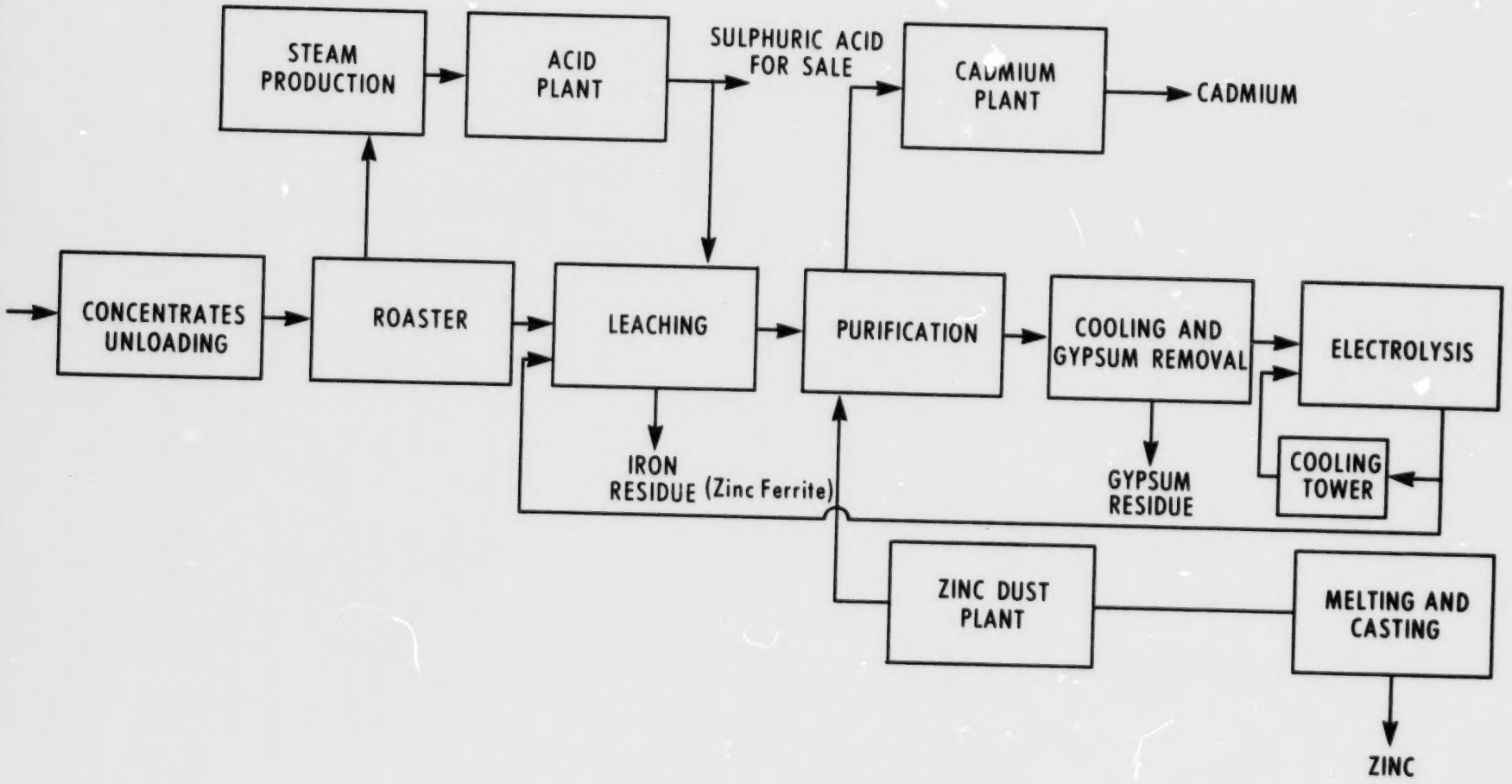

FIGURE 5 PRIMARY ZINC PLANT FLOW DIAGRAM

TABLE 3 PARTICLE SIZE DISTRIBUTION FOR PARTICULATE EMISSIONS FROM PRIMARY ZINC SMELTERS

Source	Particle size (microns)	Weight of particulates (%)
Zinc dross	>5	27
	<5	73

2.4.1 Process Description. The manufacture of iron and steel comprises some or all of the following steps.

Iron Ore Pretreatment. In certain cases iron ore is pretreated prior to the blast furnace operation. This process usually involves ore concentration followed by either sintering or pelletizing.

Iron Production. This takes place in the blast furnace. In this process, the iron-bearing materials (iron ore, sinter, pellets, mill scale, iron or steel scrap, etc.), fuel (coke), and flux (limestone and/or dolomite) are charged to the top of the furnace. Heated air (blast) and, in some instances, fuel (gas, oil or powdered coal) is blown in at the bottom. The blast air burns part of the fuel to produce heat for the chemical reactions involved and for melting the iron while the balance of the fuel and part of the gas from combustion remove the oxygen combined with the metal.

A typical blast furnace charge in Canada, per ton of product is:

Ore, Sinter, Pellets	1.6 tons
Coke	0.5 ton
Air	2.0 tons
Limestone/Dolomite	0.1 ton

The product from the blast furnace is known as either hot metal (molten) or pig iron (solid). Pig iron may be remelted with scrap in cupolas to produce cast iron.

Steel Production. Blast furnace product and steel scrap are charged to the steel furnace, where further refinement takes place. Careful control of the levels of contaminants such as silica, phosphorus, sulphur and carbon is necessary to impart the desired mechanical and chemical characteristics to the product steel. Chemical and mechanical properties may be changed by alloying with other metals, such as nickel, chromium and manganese.

The steel furnaces used in Canada in 1972 were the basic oxygen, the basic open hearth and the electric arc, listed in decreasing order of overall production capacity. Open hearth furnaces are becoming obsolete and should eventually be replaced by basic oxygen furnaces. The availability of cheap hydroelectric power in certain areas may sometimes favour the use of electric furnaces.

Steel Finishing. This includes a large number of operations, depending on the required final product. The required product shape may be achieved by casting, or in rolling mills, bar mills, and railing mills. Other processes such as scarfing, pickling and galvanizing are employed to achieve desired surface properties.

2.4.2 Emissions. The main points of manganese emission are iron ore pretreatment plants processing ores of relatively high manganese content (about 2%) and blast furnace and steel furnace operations. Only some iron ores used in Canada contain appreciable amounts of manganese and these are found mainly in Northern Ontario, around the Michipicoten region. It is estimated that about 2.5 million tons of sinter were produced from high-manganese-content ores in 1972. Emissions are usually controlled by cyclones. Steel finishing operations are conducted at relatively low temperatures where the steel is heated only to the point where it can be rolled or formed. Manganese emissions from these operations are assumed to be negligible.

Some of the companies surveyed reported test data on manganese emissions. Others reported measurements of total particulate emissions. Still others gave manganese emissions based on mass balance calculations. A previous study (10) gives uncontrolled emission factors for manganese. Emission factors developed in this study and those found in the literature (10) are summarized in Table 4.

Emission estimates are based on (in order of preference)

- source testing data on manganese emissions;
- extrapolation from average data reported by other surveyees; and
- previously published emission factor data.

Total estimated manganese emissions from primary iron and steel production in 1972 are shown in Table 5.

2.4.3 Particle Size Distribution. Some companies reported measured particle size data, as summarized in Table 6.

2.5 Iron and Steel Foundries

It is estimated that 737 567 tons of iron and steel castings were produced in Canada in 1972 (11).

2.5.1 Process Description. Scrap iron and steel are melted in different types of furnaces and cast in molds, usually made of sand. Cupola, electric induction and electric arc are the furnace types normally used for melting in iron and steel foundries.

2.5.2 Emissions. Most of the companies responding to the survey have emission control equipment, usually cyclones, baghouses or wet caps.

An uncontrolled manganese emission factor of 0.25 lb manganese/ton of process weight was derived from a previous study of particulate and zinc emissions from five Ontario foundries (12). The

TABLE 4 UNCONTROLLED MANGANESE EMISSION FACTORS FOR THE PRIMARY IRON AND STEEL INDUSTRY

Source	Uncontrolled manganese emission factor (lb Mn/ton product)	
	This report[a]	Reference 10[b]
Sinter plant*	2.9	none
Blast furnace	0.033	0.8
Open hearth with oxygen lancing	0.6[b]	0.6
Basic oxygen furnace	0.276	1.0
Electric furnace with oxygen lancing	1.51	0.3

a Based on questionnaire replies.

b Taken from reference 10 (values based on engineering judgement).

* Valid only for plants processing ores with a manganese content greater than 2%.

degree of emission control on a provincial basis was estimated internally (13). A similar study made in the United States (10) estimates the uncontrolled manganese emission factor for foundries to be 0.3 lb manganese/ton of process weight, which is comparable with the Canadian value.

Total manganese emissions to the atmosphere for 1972 are estimated at 36 tons.

2.5.3 Particle Size Distribution. Only one company provided particle size distribution data, which is presented in Table 7 together with additional data on particle size analysis of dust from gray iron cupolas in the United States (14).

2.6 Miscellaneous Industrial Sources

The survey identified many operations which either process manganese or manganese compounds or have manganese introduced into the process as an impurity in the raw materials.

2.6.1 Nonferrous Alloy Production. Manganese metal, usually in the form of powder, is used for the manufacture of copper, aluminum, and magnesium alloys. The quantity consumed by the nonferrous

TABLE 5 MANGANESE EMISSIONS FROM PRIMARY IRON AND STEEL PRODUCTION, 1972

Process stage	Manganese emissions (tons)
Iron ore pretreatment	1111
Blast furnaces	32
Steel furnaces	1281
TOTAL	2424

TABLE 6 PARTICLE SIZE DISTRIBUTION FOR PARTICULATE EMISSIONS FROM ELECTRIC ARC STEELMAKING FURNACES

Source	Particle size (microns)	Weight of particulates (%)
Electric furnace	<5	20-50
	5-10	30-50
	10-20	10-25
	>20	5-10
Electric furnace with oxygen lance	0.2-5	95

metal industry is estimated at 1285 tons. Approximately 96% is used for aluminum alloys. Aluminum alloying is done mainly by the primary aluminum producers.

TABLE 7 PARTICLE SIZE DISTRIBUTION FOR PARTICULATE EMISSIONS FROM IRON AND STEEL FOUNDRIES

Source	Particle size (microns)	Weight of particulates (%)
Canadian foundry	0.01 - 0.1	5.0
	0.1 - 1.0	20.0
	1.0 - 10.0	75.0
American foundry	0.0 - 5.0	21.2
	5.0 - 10.0	6.5
	10.0 - 20.0	7.5
	20.0 - 44.0	17.4
	> 44.0	47.4

No emissions of manganese from the alloying industry were reported. The uncontrolled emission factor for a similar survey in the United States is 12 lb manganese/ton of manganese processed (4). Based on this emission factor the total uncontrolled quantity of manganese emitted by the nonferrous alloy industry in 1972 is 8 tons.

2.6.2 Bronze Foundries. A number of bronze foundries cast manganese bronze. The manganese bronze is supplied by ingot manufacturers and is covered in section 2.6.1. It is estimated that approximately 50 tons of manganese were used in the production of manganese bronze in 1972.

It is assumed that the uncontrolled emission factor for the nonferrous alloy industry, of 12 lb manganese/ton of manganese processed (4), also applies to bronze foundries. The total uncontrolled emissions from manganese bronze foundries for 1972 are estimated at less than 1 ton.

2.6.3 Welding rod manufacture and use. No figures were available on the quantity of manganese used in the manufacture of welding rods in Canada in 1972; however, an estimated 360 tons of manganese compounds, as manganese, were used. This estimate was prorated from the quantity of manganese consumed in the United States for welding rod manufacture.

Some welding rod manufacturers do not have a melting operation but draw and cut steel wire to form rods and coat the rods with flux. Manganese and manganese compounds are used in both welding rods and fluxes. Emissions occur during the melting operation that produces the core and also from the drying and baking of the fluxes on the rods.

None of the companies surveyed gave any emission information. A survey in the United States (4) gives an emission factor of 16 lb manganese/ton manganese processed. No information on losses of manganese to the atmosphere from welding operations was found. It is assumed that another 16 lb manganese/ton manganese in the welding rods is lost from welding operations.

Total emissions of manganese from welding rod manufacture and use in 1972 are estimated at 6 tons.

2.6.4 Battery Manufacture. During 1972 the total Canadian consumption of manganese dioxide for battery manufacturing was 1633 tons (15). Two companies responded to the survey. Their combined manganese dioxide consumption is approximately 73% of the total.

Manganese dioxide is used as a depolarizer in the manufacture of manganese alkaline batteries and manganese is emitted only during the manufacture of depolarizer pellets. Based on a reply from one company, manganese emissions are estimated at less than 1 ton. Both companies report having a baghouse.

A report published in the United States gives an uncontrolled emission factor of 10 lb of manganese/ton manganese processed for the processing of manganese dioxide depolarizer pellets. The controlled emission factor for this survey is calculated to be 0.44 lb manganese/ton manganese processed. Assuming a baghouse efficiency between 96%-99%, these emissions factors are in close agreement.

2.6.5 Primary Lead Production. In 1972 two primary lead producers in Canada produced a total of 204 452 tons of lead. Questionnaire information indicates that manganese concentrations in the ores range from 0.02%-0.11%.

Manganese emissions from lead smelting operations are negligible. Some manganese is emitted from the zinc oxide fume leaching plant which is used at one plant to recover zinc from the slag.

Total emissions of manganese from primary lead production for 1972 are estimated at less than 0.1 ton.

2.6.6 Metallurgical Coke Manufacture. There were seven coke manufacturing companies in Canada in 1972 with a total coke production of 5.2 million tons (16).

It is assumed that most of the manganese contained in coal is volatilized during coking and removed in the scrubbing/cooling towers. Therefore, manganese emissions to the atmosphere could only occur during coal handling operations. Because these are low-temperature processes, the content of the particulate emissions would be similar to that of coal. It has been reported (17) that about 1.5 lb of particulates are emitted to the atmosphere per ton of coke produced and the manganese content of coal is about 26 ppm (4); therefore, total emissions from coke manufacturing in 1972 are estimated at less than 1 ton.

2.6.7 Mining Operations. No manganese ore deposits were mined in Canada in 1972 (1); however, manganese was reported in Canadian ores in concentrations up to 2% (from questionnaire returns). Usually the manganese concentration is less than 0.2%.

Particulate emissions occur during blasting, drilling and ore transport but the manganese content of any dust generated is small and manganese emissions are assumed negligible.

2.6.8 Brick and Tile Plants. It is estimated from data reported in the questionnaires and from the literature (18) that 4000 tons of manganese dioxide and 20 tons of manganese chloride were consumed by brick and tile plants during 1972. None of the companies reported any emission of manganese and no emission factors for this type of operation were found in the literature. A conservative estimate is that 1 lb of manganese is emitted per ton of manganese dioxide handled and that manganese is emitted only from handling operations. Emissions of manganese to the atmosphere in 1972 from brick and tile plants are therefore estimated at 2 tons.

2.6.9 Miscellaneous Chemicals. Statistics Canada (2, 3) did not report the manufacture of any manganese chemicals in Canada in 1972.

2.6.10 Petroleum Refining. The data received provide no evidence to indicate that manganese is discharged to the atmosphere during the refining process; however, manganese is found in light oils (distillate) and heavy oils. When these oils are burned as fuels, it is likely that the manganese is discharged with the combustion products. These emissions are described in sections 3 and 4.

Manganese emissions from miscellaneous industrial sources are summarized in Table 8.

3 EMISSIONS FROM FUEL COMBUSTION - STATIONARY SOURCES

Stationary sources can be divided into the following categories:

- Power generation
- Industrial and commercial
- Domestic

The five principal fuel types used are gaseous (natural gas, propane, etc.) diesel oils, light oils, heavy oils and coal. Of these, only light oils, heavy oils and coal contain manganese (19,20).

Emission factors used for these fuels are based on reports by the U.S. Environmental Protection Agency (4,10) and are listed in Table 9.

3.1 Power Generation

In 1972, electricity generated by coal-operated facilities accounted for 62% of total thermal generation; petroleum fuels were responsible for 10%, natural gas for 15.7% and nuclear fuels for 12.3% (21).

TABLE 8 MANGANESE EMISSIONS FROM MISCELLANEOUS INDUSTRIAL SOURCES, 1972

Source	Manganese emissions (tons)
Nonferrous alloy production	8
Bronze foundries	<1
Welding rod manufacture and use	6
Battery manufacture	<1
Primary lead production	<0.1
Metallurgical coke manufacture	<1
Mining operations	negligible
Brick and tile plants	2
Miscellaneous chemicals	negligible
Petroleum refining	0
TOTAL	16 (approx.)

Estimates of manganese emissions from power generation are listed in Table 10.

Roughly 60% of the emissions occur during the winter months (20), depending on climate and the extent to which electricity is used for heating purposes.

3.2 Industrial and Commercial

Approximately 6.5 million barrels of light fuel oil, 90 million barrels of heavy oil and 2.7 million tons of coal were consumed for industrial and commercial purposes in Canada during 1972. The figure of 2.7 million tons of coal does not include coal used for coke manufacture (see section 2.6).

Estimates of manganese emissions resulting from the combustion of industrial and commercial fuels during 1972 are listed in Table 11.

TABLE 9 MANGANESE EMISSION FACTORS FOR FUELS

Fuel	Emission factor (uncontrolled)
Light oil	0.0002 lb manganese/1000 Imp. gal.
Heavy oil	0.0005 lb manganese/1000 Imp. gal.
Coal	0.0078 lb manganese/ton

TABLE 10 MANGANESE EMISSIONS FROM POWER GENERATION, 1972

Source	Manganese emissions (lb)	(tons)
Light fuel oil	negligible	negligible
Heavy oil	159	<1
Coal	15 694	8
TOTAL	15 853	8

Heavy oil is used throughout the year for process heating. In the winter, however, it is also used for plant heating, and causes an increase in manganese emissions.

3.3 Domestic

Light oils are generally used for domestic heating. A small quantity of heavy oils are used, mainly for apartment complexes.

Approximately 81 million barrels of light fuel oil and 3 million barrels of heavy oil were used for domestic heating in 1972. Emissions occur mainly in the winter months (October - April).

Estimated manganese emissions from domestic sources in 1972 are listed in Table 12.

TABLE 11 MANGANESE EMISSIONS FROM INDUSTRIAL AND COMMERCIAL FUEL USE, 1972

Source	Manganese emissions (lb)	(tons)
Light oil	47	negligible
Heavy oil	1 518	<1
Coal	21 099	11
TOTAL	22 664	11

TABLE 12 MANGANESE EMISSIONS FROM DOMESTIC FUEL USE, 1972

Source	Manganese emissions (lb)	(tons)
Light fuel oil	566	<1
Heavy oil	53	<1
TOTAL	619	<1

4 EMISSIONS FROM TRANSPORTATION SOURCES

4.1 Motor Vehicles

Motor vehicles use either gasoline or diesel oil as fuel, neither of which contain manganese(4,10).

4.2 Rail Transport

Rolling stock use diesel oil or gasoline, neither of which contain manganese (4,10). Although the railway companies purchase heavy oils and coal, these are employed for heating and power generation and the emissions are consequently dealt with in section 3 of this report.

4.3 Shipping

Shipping uses bunker oil which contains manganese (4,10). It is estimated that only 20% of the bunker oil is burned within Canadian territory. The remainder is burned on the high seas and is not included in this inventory. Approximately 11 million barrels of bunker oil were purchased in Canada in 1972 (22). Emissions were estimated using an uncontrolled emission factor of 0.0005 lb manganese/1000 Imperial Gallons (see section 3). Emissions are substantially reduced during winter months when some inland waterways are closed.

Emissions of manganese from shipping operations in Canada for 1972 are estimated at 39 lb.

4.4 Aviation

Aircraft are fuelled with either aviation gasoline or kerosene, neither of which contain significant quantities of manganese.

5 EMISSIONS FROM SOLID WASTE INCINERATION

In 1972, approximately 1.4 million tons of refuse were disposed of in 17 municipal incinerators (23) and about 134 000 tons of sewage sludge were incinerated in three cities (23).

A previous study indicates that the uncontrolled manganese emission factor for solid waste incinerators is 0.03 lb/ton of refuse burned (10). Based on this factor it is estimated that 16 000 lb or 8 tons of manganese were discharged to the atmosphere during 1972 from municipal solid waste incinerators. The same study (10) indicates an uncontrolled manganese emission factor for sewage sludge incinerators of about 0.005 lb/ton of sewage sludge burned. Based on this factor it is estimated that 515 lb or 0.26 ton of manganese were discharged to the atmosphere during 1972 from municipal sewage sludge incinerators.

6 EMISSIONS FROM PESTICIDE APPLICATION

Maneb and Mancozeb were the main manganese containing pesticides used in Canada in 1972, and accounted for virtually all the manganese used in pesticides.

6.1 Uses

Both pesticides are used as fungicides and are very similar in chemical composition. The only difference is that Mancozeb contains zinc and is a superior fungicide.

Their main application is in disease control particularly of tomato and potato blights. They are usually applied as wet sprays. Some forms of these compounds are also used to coat potato seed pieces and cereal seeds.

6.2 Emissions

When considering the emissions resulting from the use of pesticides it is very important to delineate the parameters that determine the percentage 'drift' (drift being the amount of pesticide leaving the target area). The factors that affect drift are droplet size of the liquid, wind speed, temperature, foliage density, humidity, and operator skill.

Pesticide application is dependent upon chemical makeup and desired effect. Aerial application is used for treatment of large areas such as forests. Fruit tree spraying is usually from the operator upward whereas spraying of vegetable crops is from the operator downward. Fogging is used in certain cases that can take advantage of drifting. Application of pesticides is usually completed by July.

Losses during aerial application range from 10%-50% depending on the factors mentioned above. In fruit tree spraying the air emission may be 50% early in the season when the leaves are small. As the leaf cover increases, loss from drift decreases rapidly (24). Other types of application have an average loss of about 10% (25).

Both potato and tomato spraying are done in a downwind direction close to ground level. Emissions are therefore assumed to be small. Based on a 10% drift loss, manganese emissions are estimated at 15 tons as shown in Table 13.

TABLE 13 MANGANESE EMISSIONS FROM PESTICIDE APPLICATION BASED ON 10% DRIFT LOSS, 1972

Pesticide name	Manganese content (%)	Quantity sold (tons)	Estimated quantity applied as wet spray (tons)	Manganese emissions (tons)
Maneb[a]	16.5	497	361	6
Dithane	1.6	52	36	negligible
Mancozeb[b]	16.0	600	550	9
TOTAL				15

a Alternative names: MEB, MnEBD, Manzate Maneb, Dithane M-22.
Chemical name: Manganous ethylene bisdithiocarbonate

b Alternative name: Dithane M-45
Also includes Dikat, Manzate 0, Manzate 200.

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APPENDIX - SURVEY OF QUESTIONNAIRE RETURNS AND QUALITY INDEX

Sector	No. of questionnaires Sent	/ Returned	Rate of response (%)	Quality index of questionnaires returned* 1	2	3	4	5	Average quality index
Primary copper & nickel & assoc.	13	12	92	–	–	–	4	8	4.7
Primary iron & steel	45	28	62	2	2	5	7	12	3.9
Primary aluminum	6	6	100	–	–	–	–	6	5.0
Primary lead & zinc	6	6	100	–	–	–	–	6	5.0
Copper, brass & bronze foundries	84	27	32	2	4	7	8	6	3.4
Die casting	91	51	56	4	18	14	10	5	2.9
Iron & steel foundries	194	88	45	10	16	25	24	13	3.2
Metallurgical coke	7	3	43	–	–	1	–	2	4.7
Phosphate fertilizers & elemental phosphorus	31	28	90	–	1	13	2	12	3.9
Galvanizing	46	26	57	2	3	10	10	1	3.2
Plating	83	25	30	7	9	3	6	–	2.3
Ferroalloys & assoc.	13	4	31	–	–	–	1	3	4.8
Pesticides	58	26	45	9	10	–	4	3	2.3
Ceramics and glass	105	44	42	1	8	6	18	11	3.7
Nonferrous alloys	20	11	55	1	2	–	5	3	3.6
Battery mfg.	5	2	40	–	–	–	1	1	4.5
Rubber mfg.	24	20	83	–	2	5	7	6	3.9
Zinc oxide mfg.	2	1	50	–	–	–	–	1	5.0
Mining	39	21	54	2	2	4	5	8	3.7
Porcelain & enamels	30	17	57	4	4	4	3	2	2.7
Clay products mfg.	57	21	37	7	4	3	4	3	2.6
Petroleum refining	47	35	74	4	5	11	–	15	3.5
Vinyl stabilizers & plasticizers	13	8	62	–	–	2	3	3	4.1
Welding rod mfg.	12	10	83	2	2	–	2	4	3.4
Miscellaneous	16	13	81	–	–	4	3	6	4.2
TOTAL	1047	533	51	57	92	117	127	140	3.4

* A Quality Index of Questionnaires returned was based on the following rating:

1. No emissions reported, no backup given
2. No pertinent information
3. Poor reply, insufficient data
4. Medium reply, emissions can be calculated
5. Good reply, emissions data given and documented